

The density matrix renormalization group method. Application to the PPP model of a cyclic polyene chain.

G. Fano, F. Ortolani[†] and L. Ziosi
Dipartimento di Fisica, Università di Bologna
Via Irnerio 46, 40126 Bologna - Italy
fano@bologna.infn.it

[†]Present address: International Centre for Theoretical Physics,
Trieste, Italy
(February 1, 2008)

The density matrix renormalization group (DMRG) method introduced by White for the study of strongly interacting electron systems is reviewed; the method is variational and considers a system of localized electrons as the union of two adjacent fragments A, B . A density matrix ρ is introduced, whose eigenvectors corresponding to the largest eigenvalues are the most significant, the most probable states of A in the presence of B ; these states are retained, while states corresponding to small eigenvalues of ρ are neglected. It is conjectured that the decreasing behaviour of the eigenvalues is gaussian. The DMRG method is tested on the Pariser-Parr-Pople Hamiltonian of a cyclic polyene $(CH)_N$ up to $N = 34$. A Hilbert space of dimension $5. \times 10^{18}$ is explored. The ground state energy is $10^{-3} eV$ within the full CI value in the case $N = 18$. The DMRG method compares favourably also with coupled cluster approximations. The unrestricted Hartree-Fock solution (which presents spin density waves) is briefly reviewed, and a comparison is made with the DMRG energy values. Finally, the spin-spin and density-density correlation functions are computed; the results suggest that the antiferromagnetic order of the exact solution does not extend up to large distances but exists locally. No charge density waves are present.

I. INTRODUCTION

A few years ago White¹ introduced in the study of electron correlation a new and powerful numerical method: the density matrix renormalization group (DMRG). The method provided extremely accurate results in the case of the one-dimensional Heisenberg and Hubbard models¹⁻⁵, Hubbard-like models with bond alternation⁶ and recently has been applied to some two dimensional models^{7,8}.

DMRG is a new variational method that promises to be very useful in quantum chemistry. It deals with the main difficulty of this kind of calculations, i.e. the exponential increase of the dimension of the Hilbert space with the size of the system, in a new, direct and efficient way. While the usual packages of ab initio quantum chemistry cut the dimension of the Hilbert space by neglecting the coefficients of the configuration interaction expansion below a certain threshold, the DMRG obtains an analogous result with a different strategy. A system of localized electrons is partitioned in two blocks A, B (sometimes B is called "environment" or "universe") and all the many-electron states corresponding to situations in which the population of the two blocks is unphysical (e.g. all electrons in A , no electrons in B) are automatically truncated by the formalism. A density matrix is introduced, whose eigenvectors, corresponding to the larger eigenvalues, are the most significant, the most probable states of A in the presence of B .

These states are retained, and states corresponding to very small eigenvalues are neglected. The two blocks are

taken initially small and increase their size in the course of the calculation. As a result of the systematic truncation mentioned above, the time of computation does not grow more than the fourth power of the size of the system, keeping constant the number m of retained eigenvectors of the density matrix. The error⁹ is an exponentially decreasing function of m .

The method is especially suited to treat systems with translational or reflection invariance, since in an intermediate stage of the calculation wave functions suitable to describe the block B can be obtained simply by translation (or reflection) from those of block A .

A good candidate in order to test the method in quantum chemistry is provided by the Pariser-Parr-Pople model of conjugated polyenes. Many considerations are in favour of this choice:

- A cyclic polyene $(CH)_N$ with the carbon atoms at the vertices of a regular polygon is "translationally" invariant (here translation means a rotation of the circle circumscribed to the polygon); hence the simplification mentioned above can be applied.
- Exact full configuration interaction calculations are available^{10,11}, and we can compare the DMRG ground state energy values with these results. The comparison can be made up to $N = 18$. A further comparison can be made with the coupled cluster (CC) method¹². However, the DMRG method is much more powerful; we have computed without much effort ground state energy values up to $N = 34$ carbon atoms. The full CI Hilbert space

corresponding to $N = 34$ has dimension equal to $\binom{34}{17}^2 \approx 5.44 \times 10^{18}$.

- Trans-polyacetylene presents interesting experimental and theoretical problems: the bond alternation (and in particular the values of the two bond lengths) can in principle be deduced by ab initio computations but this problem meets considerable difficulties. Recently an interesting approach to the problem of the dimerization of polyacetylene using the DMRG method has been put forward by M.B.Lepetit and G.M.Pastor¹³; these last authors treat accurately the hopping term allowing a dependence on the distance between the C atoms and describe the electron interaction by a Hubbard term. Therefore it would be of interest to extend their work by substituting a PPP interaction to the Hubbard interaction. In the present paper we show that this extension is possible (but we do not derive the hopping term from ab initio calculations).
- The unrestricted Hartree-Fock solutions of the PPP model Hamiltonian present spin density waves and charge density waves^{14–17}. It is of interest to know whether or not these waves persist after a more precise variational approximation to the ground state (like the DMRG) is performed.

The paper is organized as follows: in Sec.2 the PPP Hamiltonian is written down and the DMRG method is reviewed. In particular we point out some mathematical aspects of the DMRG method that usually are not sufficiently emphasized. In Sec.3 the properties of the unrestricted (spin density wave) Hartree-Fock solution are briefly discussed. In Sec.4 the numerical results and the conclusions are presented.

II. THE PPP HAMILTONIAN AND THE DMRG METHOD.

The Pariser-Parr-Pople Hamiltonian of the π electronic model of a cyclic polyene $C_N H_N$ can be written as^{12,14,18}:

$$H = \beta \sum_{\langle \mu\nu \rangle} \hat{E}_{\mu\nu} + \frac{1}{2} \sum_{\mu, \nu=0}^{N-1} \gamma_{\mu\nu} (\hat{n}_\mu - 1) (\hat{n}_\nu - 1) \quad (2.1)$$

where $\hat{E}_{\mu\nu}$ are the generators of the unitary group summed over spin, and $\hat{n}_\mu = \hat{E}_{\mu\mu}$ is the occupation number of the site μ ; β , $\gamma_{\mu\nu}$ are parameters of the model, and $\langle \mu\nu \rangle$ denotes summation restricted to nearest neighbor. We limit ourselves to the series $N = 2n = 4\nu + 2$, $\nu = 1, 2, \dots$, where N denotes the total number of electrons which is equal to the total number of sites. According to ref. [12] we take $\beta = -2.5$ eV, and for the Coulomb repulsion we use the Mataga-Nishimoto prescription¹⁹:

$$\gamma_{\mu\nu} = \frac{1}{\gamma_0^{-1} + d_{\mu\nu}} \quad (\text{a. u.}) \quad (2.2)$$

where $\gamma_0 = 10.84$ eV, $d_{\mu\nu}$ denotes the distance between the vertex μ and the vertex ν of a regular polygon of N sites and is given by

$$d_{\mu\nu} = b \frac{\sin(\mu - \nu) \frac{\pi}{N}}{\sin \frac{\pi}{N}} \quad (2.3)$$

and b , the nearest-neighbor separation, is equal to 1.4 Å.

Let's see now how the DMRG method can be applied to the PPP model. We will also review briefly the principal formal and physical ideas^{1,2,20} that are behind this new and powerful numerical method.

Let A and B denote two adjacent subsets of respectively N_A , N_B sites. The method consists of two parts: step 1, called the "infinite system method" and step 2, called the "finite system method". In step 1, $N_A + N_B < N$, $N_A = N_B$ and N_A , N_B are progressively increased up to reach the condition $N_A + N_B = N$, while in step 2, we have always $N_A + N_B = N$, with variable N_A and N_B . For instance in step 1 we can have $N = 18$, $A = \{1, 2, \dots, 6\}$, $B = \{7, 8, \dots, 12\}$, in step 2 we can have $A = \{1, 2, 3, 4\}$, $B = \{5, 6, \dots, 18\}$. The main task of the method is to find a reduced set of "localized" many particle states for subsets (blocks) A and B suitable to describe the union $A \cup B$.

Let us denote by A^+ , B^+ polynomials in the creation operators corresponding to sites in A , B , respectively. Let $|0\rangle$ denote the vacuum, and let $|a\rangle = A^+|0\rangle$, $|b\rangle = B^+|0\rangle$. Clearly $|a\rangle$, $|b\rangle$ represents states of electrons localized in different subsets. We can form the state $A^+B^+|0\rangle$; this state is similar but not identical to the tensor product $|a\rangle \otimes |b\rangle$ since the operators A^+ , B^+ do not necessarily commute. We use the notation $|a\rangle|b\rangle$ to denote the compound state $A^+B^+|0\rangle$. Clearly, varying the polynomials A^+ , B^+ in all possible independent ways, the states $|a\rangle|b\rangle$ generate the whole Hilbert space.

TABLE I. Energy results: the energies (in eV) calculated via Restricted and Unrestricted HF, FCI^a and DMRG are compared for different values of N . $m_A^{(n)}$ indicates the number of states kept in block A during the the n -th DMRG iteration.

N	E_{RHF}	E_{UHF}	E_{FCI}^a	E_{DMRG}	$m_A^{(1,2)}$	$m_A^{(3)}$
6	-11.358325	-11.358325	-12.722033	-12.722032	256	512
10	-17.441467	-17.910422	-20.060503	-20.060503	256	512
14	-23.731302	-24.924267	-27.671391	-27.671333	256	512
18	-30.101389	-32.007998	-35.385430	-35.384861	256	512
22	-36.513220	-39.105943	-	-43.145027	256	512
26	-42.950070	-46.207715	-	-50.928028	256	512
30	-49.403281	-53.310920	-	-58.715323	200	400
34	-55.867856	-60.414852	-	-66.509902	200	400

^aFrom Ref. [10,11].

Suppose that we have found an exact or approximate ground state $|\psi\rangle$ of $N_A + N_B$ electrons in the subset $A \cup B$ of the chain; let us expand $|\psi\rangle$ as:

$$|\psi\rangle = \sum_{IJ} \psi_{IJ} A_I^\dagger B_J^\dagger |0\rangle \quad (2.4)$$

where $\{A_I^\dagger |0\rangle\}$ denote a complete orthonormal set of states of electrons localized in A , and $\{B_J^\dagger |0\rangle\}$ is an analogous complete set of states corresponding to B . For instance, initially we can have $A_I^\dagger B_J^\dagger |0\rangle = a_{i_1}^\dagger a_{i_2}^\dagger \dots a_{N_A}^\dagger b_{j_1}^\dagger b_{j_2}^\dagger \dots b_{N_B}^\dagger |0\rangle$ where the a^\dagger , b^\dagger create electrons in A , B respectively; in this case the numbers ψ_{IJ} are the usual configuration interaction (CI) coefficients. In principle the sums \sum_I , \sum_J run over 4^{N_A} , 4^{N_B} states respectively, since the occupation numbers n_\uparrow, n_\downarrow of a site can have four possible values: $(0,0)$, $(1,0)$, $(0,1)$, $(1,1)$. However the number of spin up electrons and the number of spin down electrons are good quantum numbers and can be fixed; we can choose states $A_I^\dagger |0\rangle$, $B_J^\dagger |0\rangle$ with fixed numbers of spin up and spin down electrons, and the coefficients ψ_{IJ} vanish unless this conservation law is fulfilled. Furthermore, during the iteration procedure, the number of states will be truncated; therefore in the expansion (2.4) we keep in general only m_A states for the block A and m_B states for the block B . In the following we shall assume that the coefficients ψ_{IJ} are real.

The main mathematical tool of the DMRG theory is provided by the following density matrix:

$$\rho_{II'} = \sum_J \psi_{IJ} \psi_{I'J} = (\psi \psi^T)_{II'} \quad (2.5)$$

The dimension of the matrix ρ is $m_A \times m_A$; however, because of the number conservation laws described above, the matrix is actually in block form: the number of up and down electrons of the states I and I' must be the same. Furthermore ρ is a non negative square matrix.

Let us first make some simplifying assumptions, that will be relaxed in the following. Let's assume that the blocks A and B are described by the same number of states ($m_A = m_B$), so that the matrix ψ is a square matrix. Denoting by S the square root of ρ ($\rho = \psi \psi^T = S^2$, $S = \rho^{1/2}$), we have the polar decomposition

$$\psi = S U_1 \quad (2.6)$$

where U_1 is an orthogonal matrix. We diagonalize S by writing $S = U D U^T$, where U is an orthogonal matrix and D is diagonal. Therefore we can write

$$\psi = U D U^T U_1 = U D V^T \quad (2.7)$$

where V is an orthogonal matrix, and $\rho = U D^2 U^T$.

Actually formula (2.7) holds for *any* rectangular matrix $m_A \times m_B$ ψ (see e.g [22]). U and D are square matrices $m_A \times m_A$ and V^T is $m_A \times m_B$. These matrices verify the conditions:

$$U^T U = I; \quad V V^T = I;$$

$$\psi \psi^T = U D^2 U^T; \quad \psi^T \psi = V D^2 V^T \quad (2.8)$$

and D is diagonal and non-negative. Let us denote by D_α the eigenvalues of D . Substituting (2.7) into (2.4) we obtain:

$$|\psi\rangle = \sum_{\alpha} D_{\alpha} |u_{\alpha}\rangle |v_{\alpha}\rangle \quad (2.9)$$

where

$$|u_{\alpha}\rangle = \sum_I U_{I\alpha} A_I^\dagger |0\rangle, \quad |v_{\alpha}\rangle = \sum_J V_{J\alpha} B_J^\dagger |0\rangle \quad (2.10)$$

What is the meaning of $|u_{\alpha}\rangle$, $|v_{\alpha}\rangle$? They represent states of the subsystems A , B , such that the probability for the whole system $A \cup B$ to be found in the state $|u_{\alpha}\rangle |v_{\alpha}\rangle$ is D_{α}^2 . The main idea of the DMRG method consists in neglecting, in Eq.(2.9), all eigenvalues D_{α} below a certain threshold which amounts to keeping only a small number m of terms in the sum (2.9) and using the corresponding states $|u_{\alpha}\rangle$ as a basis for the description of block A . Since $\text{Tr} \psi \psi^T = \sum_{\alpha} D_{\alpha}^2 = 1$, this approximation is good if the probabilities D_{α}^2 have a sufficiently rapid decrease to zero, so that $\sum_{\alpha=1}^m D_{\alpha}^2 \simeq 1$. At the best of our knowledge, all numerical experiments performed so far (see, e.g. ref. [13,21]) confirm this rapid decrease of the probabilities D_{α}^2 . Let's give an heuristic argument for this decreasing behaviour. Suppose that A_I^\dagger creates N_A^e electrons in the N_A sites of the block A , and B_J^\dagger creates N_B^e electrons in the N_B sites of the block B . In absence of the interaction, usual statistical mechanics arguments prove that the probabilities D_{α}^2 are strongly peaked about the populations $N_A^e = N_A$, $N_B^e = N_B$ (which correspond to a density of one electron per site); this is analogous to the classical result in statistical mechanics stating that the probability of distributing a large number of molecules in two communicating volumes is strongly peaked about a distribution with equal density in the two volumes.

TABLE II. Correlation energies: The correlation energies per electron (in eV) of the FCI^a and DMRG solutions with respect to the Restricted and Unrestricted HF approximations are compared for different values of N .

N	$\frac{E-E(RHF)}{N}$		$\frac{E-E(UHF)}{N}$		$m_A^{(1,2)}$	$m_A^{(3)}$
	FCI ^a	DMRG	FCI ^a	DMRG		
6	-0.227285	-0.227285	-0.227285	-0.227285	256	512
10	-0.261904	-0.261904	-0.215008	-0.215008	256	512
14	-0.281435	-0.281431	-0.196223	-0.196219	256	512
18	-0.293558	-0.293526	-0.187635	-0.187603	256	512
22	-	-0.301446	-	-0.183595	256	512
26	-	-0.306844	-	-0.181551	256	512
30	-	-0.310401	-	-0.180147	200	400
34	-	-0.313001	-	-0.179266	200	400

^aFrom Ref. [10,11].

Because of the central limit theorem, the peak is gaussian in the classical case; we make the conjecture that even in the quantum interacting case that we are considering, this gaussian behaviour still holds, at least for translationally invariant systems, like the PPP model. Of course if the conjecture is true, it explains the strongly decreasing behaviour of the probabilities D_α^2 mentioned above.

Let's now proceed with the description of the DMRG method. Once we have a pretty good basis of m_A states $|u_\alpha\rangle$ that describe the block A , and m_B states $|v_\alpha\rangle$ that describe the block B , the next task consists in the enlargement of the blocks. In the first part of the algorithm (infinite system method), since $N_A = N_B$ and the system is translationally invariant, the states $|v_\alpha\rangle$ can be simply obtained by translating the states $|u_\alpha\rangle$. Hence we can concentrate our attention on the block A .

The simplest way of enlarging the block A consists in adding a site s to A , obtaining a new block $A' = A \cup s$. White¹ denotes by $A \bullet$ this new block. Denoting by $|s_1\rangle = |0\rangle$, $|s_2\rangle = a_{s\uparrow}^\dagger|0\rangle$, $|s_3\rangle = a_{s\downarrow}^\dagger|0\rangle$, $|s_4\rangle = a_{s\uparrow}^\dagger a_{s\downarrow}^\dagger|0\rangle$, the states describing the site s , we have $4m_A$ vectors

$$A_I'^+ |0\rangle = |u_{\alpha_I}\rangle |s_{\gamma_I}\rangle, \quad I = (\alpha_I, \gamma_I) \\ \alpha_I = 1, \dots, m_A, \quad \gamma_I = 1, \dots, 4 \quad (2.11)$$

in order to describe $A' = A \bullet = A \cup s$.

At the same time, we add an analogous site t to the block B , and we consider the vectors $|v_\beta\rangle |t_\delta\rangle$ ($\beta = 1, 2, \dots, m_B$, $\delta = 1, 2, 3, 4$) in order to describe the block $B' = B \bullet = B \cup t$. With such a basis we can now proceed to compute the expansion (2.4) for the wavefunction for the new superblock $A' \cup B'$.

Let us use the term "local" to denote operators $a_\mu^\dagger, a_\mu, n_\mu$ referring to one site μ only, and the term "internal to block A " to denote operators whose site indices belong to the block A .

The idea is now to compute a new "effective" Hamiltonian matrix H' , by using the truncated basis consisting of the $16m_A m_B$ vectors $|u_\alpha\rangle |s_\gamma\rangle |v_\beta\rangle |t_\delta\rangle$.

TABLE III. Comparison of approximate solutions: The correlation energy $\frac{E-E_{RHF}}{N}$ (in eV) of the DMRG solution is compared with the partial cluster analysis ($|e^D\rangle|RHF$)^a, the Approximate Coupled Pair theory with Quadruples (ACPQ)^b and the Approximate Coupled Pair theory with Triples and Quadruples (ACPTQ)^b.

N	$ e^D\rangle RHF$ ^a	ACPQ ^b	ACPTQ ^b	DMRG	$m_A^{(1,2)}$	$m_A^{(3)}$
6	-0.224196	-0.2238	-0.2253	-0.227285	256	512
10	-0.248723	-0.2515	-0.2577	-0.261904	256	512
14	-0.256777	-0.2649	-0.2762	-0.281431	256	512
18	-	-0.2720	-0.2887	-0.293526	256	512
22	-	-0.2763	-0.2994	-0.301446	256	512

^aFrom Ref. [11].

^bFrom Ref. [12].

Clearly it is easy to compute terms of the Hamiltonian containing local operators referring only to one of the four blocks A , s , B , t ; these terms are known from previous steps of the iteration. A little more care is needed in order to compute terms like $a_\mu^\dagger a_\nu$ or $n_\mu n_\nu$ with μ, ν belonging to different blocks (e.g. $\mu \in A$, $\nu \in s$, etc.). For this purpose it is necessary to keep in the computer memory all the matrix elements of the local operators $\langle u_{\alpha_1} | a_\mu^\dagger | u_{\alpha_2} \rangle$, $\langle v_{\beta_1} | n_\nu | v_{\beta_2} \rangle$.

The entire procedure can now be repeated: we look for the ground state vector ψ' of the truncated Hamiltonian H' , by using Lanczos's or Davidson's algorithm. A new density matrix $\psi' \psi'^T$ and new state vectors $|u'_\alpha\rangle$, that represent states of A' , are computed according to the analogous of the first of formulas (2.10) which now reads:

$$|u'_\alpha\rangle = \sum_{I=1}^{4m_A} U'_{I\alpha} A_I'^+ |0\rangle \\ = \sum_{I=1}^{4m_A} U'_{I\alpha} |u_{\alpha_I}\rangle |s_{\gamma_I}\rangle \quad \alpha = 1, \dots, m_{A'} \quad (2.12)$$

Again we do not keep all the vectors: $m_{A'}$ is generally less than $4m_A$ and often one puts $m_{A'} = m_A$, although this choice is not necessary. The corresponding $|v'_\beta\rangle$ that describe B' are obtained from the $|u'_\alpha\rangle$ by translation.

In this new truncated basis we compute the matrix elements of all the local and internal operators relative to block A' and we keep them in the computer memory, in order to use them in next steps of the method. If, for example, we have an operator O internal to block A , it is also internal to the new block A' and we have the following rule to update its matrix elements:

$$\langle u'_{\alpha_1} | O | u'_{\alpha_2} \rangle = \sum_{I, I'=1}^{4m_A} U'_{I\alpha_1} \langle 0 | A_I' O A_{I'}'^+ | 0 \rangle U'_{I'\alpha_2} \\ = \sum_{I, I'=1}^{4m_A} U'_{I\alpha_1} \langle u_{\alpha_I} | O | u_{\alpha_{I'}} \rangle \langle s_{\gamma_I} | s_{\gamma_{I'}} \rangle U'_{I'\alpha_2} \\ = \sum_{I, I'=1}^{4m_A} U'_{I\alpha_1} \langle u_{\alpha_I} | O | u_{\alpha_{I'}} \rangle \delta_{\gamma_I \gamma_{I'}} U'_{I'\alpha_2}, \\ \text{for } \alpha_1, \alpha_2 = 1, \dots, m_{A'} \quad (2.13)$$

Two more sites are added to the blocks A' , B' , giving rise to new blocks $A'' = A' \bullet$, $B'' = B' \bullet$, etc. By the systematic procedure of adding two more sites, truncating the basis and updating the Hamiltonian matrix at each iteration, systems of large size can be handled.

A comment is in order about the choice of the two sites that are added and their position with respect to blocks A and B . We can form the superblock $A \bullet B \bullet$ or the superblock $A \bullet \bullet B$. White suggests that the enlarged configuration $A \bullet B \bullet$ is to be preferred to $A \bullet \bullet B$ in the case of periodic boundary conditions, the opposite holds in the case of open boundary condition. $A \bullet B \bullet$,

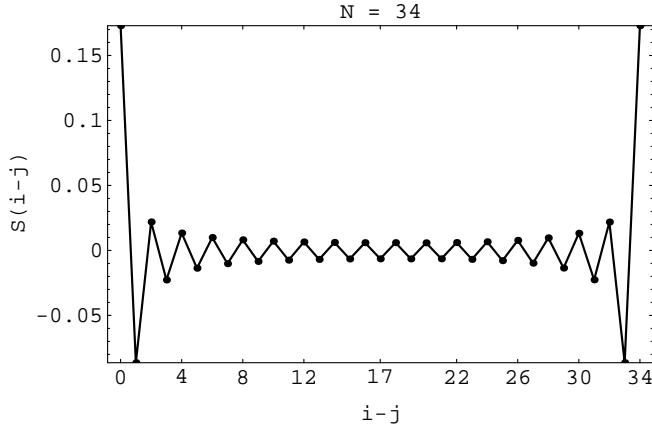


FIG. 1. Spin-spin correlation function versus the distance between sites.

In fact the blocks A and B are separated by the site t in the case while they become adjacent by periodicity in $A \bullet \bullet B$. The kinetic part of the Hamiltonian (2.1) “connects” two blocks only by its border sites with operators a_{μ}^{\dagger} , a_{ν} , whose matrix elements are known. These matrices are “big” for blocks A and B , and “little” for the 1-site blocks s and t , so the matrix elements of the hamiltonian H' are simpler when a “big” block is surrounded by 1-site blocks.

The “infinite system algorithm” is stopped when the number of sites of $A \cup B$ reaches the total number N of sites. In order to improve the accuracy of the method, White himself proposed a second algorithm, that we will briefly describe. This second algorithm takes place after the infinite system algorithm reaches the end.

In the finite system algorithm, to an increase of A by one site it corresponds a *decrease* of the “universe” B by one site. Denoting by A_x , B_y blocks A and B with x, y sites respectively, we start with the system $A_{\frac{N}{2}-1} \bullet B_{\frac{N}{2}-1} \bullet$ and we want to construct the systems $A_{\frac{N}{2}} \bullet B_{\frac{N}{2}-2} \bullet$, $A_{\frac{N}{2}+1} \bullet B_{\frac{N}{2}-3} \bullet$, etc. Therefore in order to use the translational invariance, we need to keep in the computer memory all the relevant matrix elements of $A_{\frac{N}{2}-2}$, $A_{\frac{N}{2}-3}$, etc., in order to be able to use the symmetry and produce the matrix elements of $B_{\frac{N}{2}-2}$, $B_{\frac{N}{2}-3}$, etc. It should be noticed that when $m_{B'} < m_{A'}$ (this certainly happens when B becomes small) the rows of ψ' cannot be linearly independent. As a consequence, $\psi' \psi'^T$ has many eigenvalues equal to zero.

From Eq.(2.8) we see that the $m_{A'} \times m_{A'}$ matrix $\psi' \psi'^T$ and the smaller $m_{B'} \times m_{B'}$ matrix $\psi'^T \psi'$ have the same non vanishing eigenvalues. In practice it is sufficient to diagonalize only the smallest of the two density matrices. The procedure stops when we reach the system

$A_{N-3} \bullet B_1 \bullet$, i.e. when the block B has reduced to a single site. We can now increase B and decrease A ; the subsystems A , B behave like if they were separated by a moving zipper. At every step we increase the accuracy of the states $|u_{\alpha}\rangle$ that describe the blocks A_x and after few oscillations of the zipper all the blocks A'_x , $2 \leq x \leq N-2$, accurately represent parts of a complete system of N sites, the remaining “universe” being the corresponding B'_{N-x} block.

During this procedure, all the relevant matrix elements of the local operators must be stored and updated. A more detailed explanation of this point can be found in the original paper by White². Usually one stops when A and B have the same length.

III. THE UNRESTRICTED HARTREE-FOCK (UHF) SOLUTION.

Let us still denote by $a_{\mu\sigma}^+$ the creation operator of an electron of spin σ on the site μ . The creation operator of an electron in a symmetric Bloch orbital is given by (we use letters k, k_1, k_2 .. to denote the symmetric orbitals):

$$a_{k\sigma}^+ = \frac{1}{\sqrt{N}} \sum_{\mu=0}^{N-1} e^{i\omega k\mu} a_{\mu\sigma}^+ \quad k = 0, 1, \dots, N-1 \quad (3.1)$$

where $\omega = \frac{2\pi}{N}$. In terms of these operators, the Hamiltonian can be written as

$$H = 2\beta \sum_{k\sigma} \cos(\omega k) a_{k\sigma}^+ a_{k\sigma} - E_0 + \frac{1}{2} \sum_{k_1 k_3 k\sigma\tau} K(k) a_{k_1\sigma}^+ a_{k_3+k,\tau}^+ a_{k_3,\tau} a_{k_1+k,\sigma} \quad (3.2)$$

where all k indices run from 0 to $N-1$, the constant term $E_0 = \sum_{\gamma<\nu} \gamma_{\mu\nu}$ has been added to the Hamiltonian and represents the internuclear repulsion energy, and $K(k)$ is given by:

$$K(k) = \frac{1}{N} \sum_{\mu}^{N-1} \gamma_{0\mu} e^{i\omega k\mu} \quad k = 0, 1, \dots, N-1 \quad (3.3)$$

Due to the discrete rotational symmetry of the polygon, all indices can be taken modulo N . It is convenient to represent the k indices on a circle (see fig. 1 of ref. [16]). The restricted Hartree-Fock orbitals are determined by the condition:

$$N - \nu < k < N + \nu \quad (3.4)$$

which characterizes the Fermi sea F . The restricted Hartree-Fock (RHF) single particle energies are given by¹⁵:

$$\epsilon_k = 2\beta \cos(\omega k) + NK(0) - \sum_{k_1 \in F} K(k - k_1) \quad (3.5)$$

and the total RHF energy is:

$$E_{RHF} = -E_0 + \sum_{k \in F} [2\beta \cos(\omega k) + \epsilon_k] \quad (3.6)$$

It is known since long time that it is possible to lower the RHF ground state energy by considering molecular orbitals that are linear combinations of the orbitals ϕ_k and ϕ_{k+n} corresponding to two endpoints of a diameter of the circle of Fig.1 in ref. [16].

Furthermore, taking into account also the spin indices of the two orbitals, there are many different possibilities that give rise to local minima of the UHF energy. All these possibilities have been carefully studied many years ago by Fukutome¹⁷, Paldus and Cizek¹⁵, and others, and give rise to charge density waves (CDW) and spin density waves (SDW). However in the case of the Mataga-Nishimoto prescription for the two center Coulomb repulsion integral and with the values of the parameter given in Sec.1, we have checked that the lowest UHF energy is obtained by the following BCS-Bogoliubov canonical transformation (which corresponds to the $(A^\dagger + B^\dagger)^\dagger$ case of ref. [15]):

$$\begin{aligned} \gamma_{k\uparrow} &= u_k a_{k\uparrow} + v_k a_{k+n\uparrow} \\ \gamma_{k\downarrow} &= -u_k a_{k\downarrow} + v_k a_{k+n\downarrow} \end{aligned} \quad (3.7)$$

where $u_k^2 + v_k^2 = 1$, $u_{k+n} = u_k$, $v_{k+n} = -v_k$. The operators $\gamma_{k\sigma}^\dagger$ create UHF orbitals, since the linear combination depend on σ .

The first-order density matrix (in the pseudomomenta representation) is given by:

$$\langle a_{k_1\sigma}^\dagger a_{k_2\sigma} \rangle = \delta_{k_1, k_2} f^{(1)}(k_1) + \delta_{k_1, k_2+n} f^{(2)}(k_1) (-1)^\sigma \quad (3.8)$$

where $f^{(1)}(k) = u_k^2$, $f^{(2)}(k) = u_k v_k$ for $k \in F$, and $f^{(1)}(k) = v_k^2$, $f^{(2)}(k) = -u_k v_k$ for $k \notin F$. In the original atomic-orbital basis we have the interesting formula:

$$\langle a_{\mu\sigma}^\dagger a_{\mu\sigma} \rangle = \frac{1}{2} + (-1)^{\mu+\sigma} \delta \quad (3.9)$$

where $\delta = \frac{1}{N} \sum_{k=0}^{N-1} |u_k v_k|$. This formula shows the existence of SDW of antiferromagnetic type; the occupation numbers $\langle n_\uparrow \rangle$ and $\langle n_\downarrow \rangle$ are different from each other on the same site (when one of the two is larger than $\frac{1}{2}$ the other is smaller than $\frac{1}{2}$) giving rise to a decrease of the on-site Coulomb repulsion. Furthermore no CDW appear, since $\langle n_\uparrow \rangle + \langle n_\downarrow \rangle = 1$.

The expectation value of the Hamiltonian (2.5) can be easily computed by using Wick's theorem; minimization of $\langle H \rangle$ with respect to the coefficients u_k, v_k gives rise to the following well known set of equations^{15,17} of the BCS type:

$$u_k^2 = \frac{1}{2} \left(1 + \frac{|\xi_k|}{\sqrt{\xi_k^2 + \Delta_k^2}} \right), \quad v_k^2 = \frac{1}{2} \left(1 - \frac{|\xi_k|}{\sqrt{\xi_k^2 + \Delta_k^2}} \right) \quad (3.10)$$

where $\xi_k = \frac{1}{2}(\hat{\epsilon}(k) - \hat{\epsilon}(k+n))$, and the UHF orbital energies are given by

$$\begin{aligned} \hat{\epsilon}(k) &= 2\beta \cos(\omega k) + NK(0) - \sum_{q \in F} K(k-q) u_q^2 \\ &- \sum_{q \notin F} K(k-q) v_q^2, \quad \text{for } k = 0, 1, \dots, N-1 \end{aligned} \quad (3.11)$$

and $\Delta(k)$ must fulfil the famous "gap equation":

$$\begin{aligned} \Delta(k) &= \frac{1}{2} \sum_{q \in F} [K(k-q) + K(k-q+n)] \\ &\times \frac{\Delta(q)}{\sqrt{\xi_q^2 + \Delta(q)^2}}, \quad \text{for } k = 0, 1, \dots, N-1 \end{aligned} \quad (3.12)$$

If the only solution of the gap equation is the trivial solution $\Delta(k) = 0$, we obtain simply the RHF ground state. If a non trivial solution exists, the non linear system of equations (3.10), (3.11), (3.12) can be easily solved numerically by an iterative method. Starting with $\Delta(q) = \text{constant}$ and $\hat{\epsilon}(k) = \epsilon(k)$, we solve the gap equation (3.12) by iteration. Usually 30 – 40 iterations will suffice. The solution $\Delta(k)$ is substituted into Eqs. (3.10), (3.11); in this way we obtain a set of approximate orbital energies $\hat{\epsilon}_1(k)$. The entire procedure is repeated substituting in the right hand side of Eq. (3.12) the solution $\Delta(k)$ and $\xi_k = \frac{1}{2}(\hat{\epsilon}_1(k) - \hat{\epsilon}_1(k+n))$, etc., until the entire set of equations is fulfilled with sufficient accuracy.

The UHF ground state energy of the model is given by

$$\begin{aligned} E_{UHF} &= - \sum_{k_1, k_2=0}^{N-1} K(k_2 - k_1) \\ &\times \left[f^{(1)}(k_1) f^{(1)}(k_2) + f^{(2)}(k_1) f^{(2)}(k_2) \right] \\ &- E_0 + \frac{1}{2} K(0) N^2 + 4\beta \sum_{k \in F} \cos(\omega k) f^{(1)}(k) \end{aligned} \quad (3.13)$$

The antiferromagnetic long-range order of the UHF solution appears also in the height of the peak of the magnetic structure factor:

$$\begin{aligned} S(k) &= \sum_{j=0}^{N-1} e^{-i \frac{2\pi}{N} jk} \langle S_z(j) S_z(0) \rangle \\ &= \frac{1}{4} + N \delta_{k, \frac{N}{2}} \delta^2 - \frac{1}{2N} \sum_{q=0}^{N-1} f^{(1)}(q) f^{(1)}(q-k) \\ &- \frac{1}{2N} \sum_{q=0}^{N-1} f^{(2)}(q-k-n) f^{(2)}(q) \end{aligned} \quad (3.14)$$

which is reached for $k = \frac{N}{2}$. We have :

$$S\left(\frac{N}{2}\right) = \frac{1}{4} + \frac{1}{N} \left[\sum_q |u_q v_q|^2 \right] - \frac{1}{N} \sum_q (u_q v_q)^2 \quad (3.15)$$

and this quantity scales like N for large N .

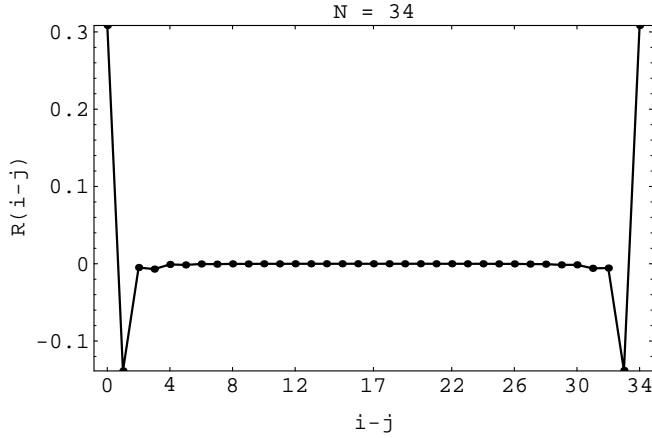


FIG. 2. Density-density correlation function versus the distance between sites.

IV. NUMERICAL RESULTS AND CONCLUSIONS

In Table I we show the energy results calculated with the DMRG method up to $N = 34$, and we compare them with RHF, UHF and FCI energies (the FCI energies are available only up to $N = 18$).

We see that the relative error of the DMRG solution with respect to FCI is only 2.1×10^{-6} for $N = 14$ and 1.6×10^{-5} for $N = 18$, which is a quite satisfactory result.

Table II shows the correlation energy per electron of the FCI and DMRG solutions with respect to the RHF and UHF approximations.

The DMRG method compares favourably with the Coupled Cluster method; in Table III the correlation energies $(E - E_{RHF})/N$ are compared with coupled cluster results of ref. [11,12]. The DMRG energy is slightly lower than the Approximate Coupled Pair with Triples and Quadruples (ACPTQ) value. All calculations were performed iterating the DMRG algorithm three times (the first iteration uses the infinite system method, the second and third iterations use the finite system method). We stop when A and B have the same length.

In the first iteration the size of the system grows, but the potential between two sites is kept equal to its final value, i.e. to the value attained when the number of sites of the polygon is N . Generally we keep 256 states in block A during both the first and the second iteration; in order to achieve a better convergence, during the third iteration we keep 512 states. In the heaviest calculations ($N = 30, 34$) we keep only 200 – 400 states in block A, due to memory/disk-space limitations. It should be noted that the disk-memory requirement grows with the number of sites even if the number of retained states is

held constant. This is due to the long range nature of the interaction that forces us to keep on disk a linearly growing number of matrices that represent the local operators. We have checked that the disk-space grows as Nm^2 .

In Fig. 1 the spin-spin correlation function $S(i-j) = \langle S_z(i)S_z(j) \rangle$ is plotted: a short range antiferromagnetic order is clearly present. We have computed the Fourier transform $S(k)$ which of course reaches its maximum value for $k = \frac{N}{2}$, like the UHF-SDW solution (see (3.14)). However, the growth is linear with N for the UHF-SDW solution, but scales approximately as $0.1398 + 0.1457 \log N$ for the DMRG solution. Therefore we cannot speak of long range SDW. Also the CDW are ruled out by the present calculation. This can be seen from the graph of the density-density correlation function

$$R(i, j) = \langle n(i)n(j) \rangle - \langle n(i) \rangle \langle n(j) \rangle \quad (4.1)$$

(see Fig. 2).

Concluding, the DMRG method provides a very powerful tool for the calculation of energies and properties of simple many electrons Hamiltonians. It gives results very close to full CI results and is able to handle Hilbert spaces of very large dimension. It would be of great interest to apply the method to a realistic many electrons Hamiltonian, possibly after a previous localization of the occupied and virtual orbitals. However, this program meets with some difficulty because of the large number of matrices that must be kept when the four orbitals of the interaction term belong to different blocks.

ACKNOWLEDGMENTS

The authors are greatly indebted to G.L. Bendazzoli for teaching them the peculiarities of the PPP model, and to A. Parola for extremely useful discussions and suggestions.

¹ S.R. White, Phys. Rev. Lett. **69**, 2863 (1992).

² S.R. White, Phys. Rev. B **48**, 10345 (1993).

³ S.R. White and D.H. Huse, Phys. Rev. B **48**, 3844 (1993).

⁴ S. Qin, S. Liang, Z. Su and L. Yu, Phys. Rev. B **52**, R5475 (1995).

⁵ S. Daul and R.M. Noack, Z. Phys. B. **103**, 293 (1997).

⁶ H. Pang and S. Liang, Phys. Rev. B **51**, 10287 (1995).

⁷ T. Xiang, Phys. Rev. B **53**, R10445 (1996).

⁸ S.R. White and D.J. Scalapino, Phys. Rev. Lett. **80**, 1272 (1998).

⁹ S. Liang and H. Pang, Phys. Rev. B **49**, 9214 (1994).

¹⁰ G.L. Bendazzoli and S. Evangelisti, Chem. Phys. Lett. **185**, 125 (1991).

- ¹¹ G. L. Bendazzoli, S. Evangelisti and L. Gagliardi, Int. J. Quantum Chem. **51**, 13 (1994).
- ¹² J. Paldus and P. Piecuch, Int. J. Quantum Chem. **42**, 135 (1992).
- ¹³ M.B. Lepetit and G.M. Pastor, Phys. Rev. B **56**, 4447 (1997).
- ¹⁴ J. Cizek and J. Paldus, J. Chem. Phys. **47**, 3976 (1967).
- ¹⁵ J. Paldus and J. Cizek, Phys. Rev A, **2**, 2268 (1970).
- ¹⁶ J. Paldus and M. Boyle, Int. J. Quantum Chem. **22**, 1281 (1982).
- ¹⁷ H. Fukutome, Progr. Theor. Phys. **40**, 998, 1227 (1968).
- ¹⁸ R.G. Parr, The Quantum theory of Molecular Electronic Structure (Benjamin, New York, 1963).
- ¹⁹ N. Mataga and K. Nishimoto, Z. Physik Chem. **13**, 140 (1957).
- ²⁰ J. Gonzalez, M.A. Martin-Delgado, G. Sierra and A.H. Vozmediano, *Quantum Electron Liquids and High- T_c Superconductivity*, Springer-Verlag, Berlin Heidelberg (1995).
- ²¹ G.L. Bendazzoli, S. Evangelisti, G. Fano, F. Ortolani and L. Ziosi, unpublished.
- ²² W.H. Press, B.P. Flannery, S.A. Teukolsky and W.T. Vetterling, *Numerical Recipes: The Art of Scientific Computing*, Cambridge University Press, New York (1986).